ADIABATIC-TO-DIABATIC ELECTRONIC STATE TRANSFORMATION AND CURVILINEAR NUCLEAR COORDINATES FOR MOLECULAR SYSTEMS

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Following an original idea of Baer, since then several times applied to various small molecular collisional systems, it is shown that – whatever the choice of *curvilinear* generalized coordinates to describe the molecular gometry and overall rotation – the algebraic framework proposed by Baer remains valid provided only that the exact tensorial expression of the kinetic energy operator is used.

A few years ago, Smith [1] introduced a procedure to transform the adiabatic electronic states into diabatic states, for the atom–atom case. Baer extended this procedure to the atom–diatom collision [2–4] and applied it successfully in various cases [5,6]. According to this procedure, the transformation matrix (called below **G**) is obtained as a solution of a first-order vector differential equation:

$$\mathbf{\nabla}\cdot\mathbf{G} + \mathbf{T}^{(1)}\mathbf{G} = 0\,, \qquad (1)$$

where $\mathbf{\nabla}$ is the vectorial covariant gradient operator in terms of N nuclear coordinates and $\mathbf{T}^{(1)}$ is a vector matrix the elements of which are antisymmetric. The matrices **G** and $\mathbf{T}^{(1)}$ have the number of electronic states into play as order (ν).

Eq. (1) has a unique solution when, and only when, each pair of the component matrices of $\mathbf{T}^{(1)}$ fulfils a special condition [2] which, in its turn, determines a special algebra for **G**. The solution was discussed for $\nu = 2$ or 3 and $N = 1$, 2 and 3 [1–8]. Finally, Baer proposed a general method enabling one to numerically obtain a solution for any value of ν and N [9], i.e. to propagate the solution from one point to another one in R^N.

In all the above cases (including ref. [3] in which the collision is elegantly treated in three dimensions by introducing various quasi-momentum operators for the angular momentum and its components, cf. eq. (3.6) in ref. [3]), the kinetic energy operators do not involve crossed quadratic terms. The purpose of the present note is to show that – whatever the set of *curvilinear* generalized coordinates to describe the molecular geometry and overall rotation and, thus, resorting to the most general expression of the kinetic energy operator [10–15]–the algebraic framework introduced by Baer remains valid.

It should be emphasized here that the adiabatic-to-diabatic transformation (starting, as usual, from finite

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dimensional AOs basis set + SCF + finite dimensional CI calculations of the adiabatic states) is not in general exact and analytic in the whole region of interest. This stems from the fact that, when a non-adiabatic coupling comes into play, the elements of matrix **G** may become either multivalued functions or, even, locally distributions. But this is unimportant. What is physically important is that, in general, a finite number ν of adiabatic states are involved and hence changing rapidly with nuclear position in the vicinity where the non-adiabatic coupling acts noticeably. What is desired is a $\nu \times \nu$ orthogonal matrix **G**, which needs not to be exact and analytic but needs to be a transformation matrix to ν wavefunctions that are approximately diabatic in this vicinity. The way in which matrix **G** is constructed is thus of secondary importance. The conditions derived below are – as Baer already pointed out in ref. [2] – necessary and sufficient to obtain a solution; not for the solution to be unique and analytic in the whole region of interest.

Let a l-atom molecular system be described in the galilean center-of-mass frame (parallel to the space fixed frame) with the help of $3l-6$ internal coordinates $q = \{q^i (i = 1,\ldots, 3l-6)\}$ and let 3 Euler angles $\Theta = \{\phi, \theta, \chi\}$ account for the angular position of the body-fixed frame relative to the center-of-mass frame. After elimination of the nuclear center-of-mass motion, the total hamiltonian reads

$$H = T^{\mathrm{nu}} + H^{\mathrm{el}} , \tag{2}$$

where T^{nu} is the nuclear kinetic operator (expressed in terms of all the $3l-3 = N$ curvilinear nuclear coordinates $Q = q \oplus \Theta$) and H^{el} the electronic hamiltonian at fixed nuclei (expressed in terms of cartesian electronic coordinates). Let us suppose the adiabatic electronic eigenstates at fixed nuclei ϕ_α ($\alpha = 1, 2,\ldots, \nu$) be known:

$$H^{\mathrm{el}}\phi_\alpha(q;\text{electrons}) = E_\alpha(q)\phi_\alpha(q;\text{electrons}) . \tag{3}$$

The total wavefunction reads [‡]

$$\Psi(Q;\text{electrons}) = \sum_{\alpha=1}^{\nu} \phi_\alpha(Q;\text{electrons})\chi_\alpha(Q) , \tag{4}$$

[‡] In eq. (4), ϕ_α depends on Q and not only on q as in eq. (3) because the electronic functions are supposed to follow the nuclear motion and may thus be rotated.

and the total Schrödinger equation $(H-E)\Psi = 0$ may, as usually, be written as a set of close-coupled equations:

$$[E_\beta(q) - E]\,\chi_\beta(Q) + \sum_{\alpha=1}^{\nu} \langle \phi_\beta(Q;\text{electrons}) T^{\mathrm{nu}} \phi_\alpha(Q;\text{electrons})\chi_\alpha(Q)\rangle = 0 , \tag{5}$$

where the bracket notation indicates integration over the electron coordinates only.

T^{nu} is expressed as (Einstein summation convention over repeated coordinate indices is used henceforth) [16]:

$$T^{\mathrm{nu}} = \tfrac{1}{2} P_i^+ g^{ij}(Q) P_j \qquad (i, j = 1, 2\ldots 3l-6, \theta, \phi, \chi; = 1, 2,\ldots, N) , \tag{6}$$

where:

$$P_i = -i\hbar\,\partial/\partial Q^i , \quad P_i^+ = P_i + \Lambda_i \qquad (i = 1, 2,\ldots, 3l-6, \theta, \phi, \chi; = 1, 2,\ldots, N) ,$$
$$\Lambda_i = -i\hbar(\partial^2 x^\alpha/\partial Q^i \partial Q^j)\partial Q^j/\partial x^\alpha \tag{7}$$

is a multiplicative operator, and $g^{ij}(Q)$ is the contravariant expression of the metric tensor of the transformation $x^\alpha = x^\alpha(Q)$, where x^α ($\alpha = 1, 2,\ldots, 3l$) denote the $3l$ mass-weighted *cartesian* coordinates of the nuclei in the center-of-mass frame. In matrix notation, $g^{ij}(Q)$ can be expressed as a $(3l-3) \times (3l-3)$ symmetrical matrix:

$$g^{ij}(Q) = \left[\begin{array}{c|c} \mathbf{D}(q) & \mathbf{B}(q)\mathbf{W}(\Theta) \\ \hline [\mathbf{B}(q)\mathbf{W}(\Theta)]^{\mathrm{T}} & \mathbf{W}^{\mathrm{T}}(\Theta)\mathbf{I}^{*-1}(q)\mathbf{W}(\Theta) \end{array}\right], \tag{8}$$

where the matrix

$$\mathbf{A}^{-1}(q) = \left[\begin{array}{c|c} \mathbf{D}(q) & \mathbf{B}(q) \\ \hline \mathbf{B}^{\mathrm{T}}(q) & \mathbf{I}^{*-1}(q) \end{array}\right]$$

is given in eq. (23) of ref. [17], and $\mathbf{W}(\Theta)$ is the 3×3 matrix transforming the classical conjugate momenta p_θ, p_ϕ, p_χ into J_x, J_y, J_z, the classical body-fixed components of the total angular momentum (cf. eq. (6), p. 282, in ref. [12]). Thus:

$$T^{\mathrm{nu}} = -\tfrac{1}{2}\hbar^2 g^{ij}(Q)\partial^2/\partial Q^i \partial Q^j - \tfrac{1}{2} i\hbar\gamma^j(Q)\partial/\partial Q^j , \tag{9}$$

where

$$\gamma^j(Q) = (P_i + \Lambda_i) g^{ij}(Q) .$$

In eq. (5), the action of T^{nu} on the products $\phi_\alpha(Q;\text{electrons})\chi_\alpha(Q)$ results – after integration over the electonic coordinates – in the following set of close-coupled equations:

$$[T^{nu} + E_\beta(q) - E]\,\chi_\beta(Q) + \sum_{\alpha=1}^{\nu} [{}^{\beta\alpha}T^{nu}(Q) - \hbar^2 {}^{\beta\alpha}T^i(Q)\nabla_i]\,\chi_\alpha(Q) = 0\,, \quad (10)$$

where $E_\beta(q)$ is the usual adiabatic potential energy surface,

$${}^{\beta\alpha}T^{nu}(Q) = \langle\phi_\beta(Q;\text{electrons})|T^{nu}\phi_\alpha(Q;\text{electrons})\rangle\,,$$

$${}^{\beta\alpha}T^i(Q) = \langle\phi_\beta(Q;\text{electrons})|\nabla^i\phi_\alpha(Q;\text{electrons})\rangle\,,$$

$\nabla^i = g^{ij}(Q)\partial/\partial Q^j$ is the ith contravariant component of the gradient vectorial operator, whereas $\nabla_i = \partial/\partial Q^i$ is the usual (covariant) component of the gradient operator.

It should be emphasized here that eq. (10) is a generalization of Baer's eq. (7) in ref. [2], but with exactly the same structure. The use of the gradient operator has just been rationalized with the help of some tensorial algebra. It should also be kept in mind that in T^{nu} and in the expressions ${}^{\beta\alpha}T^i(Q)\nabla_i$ and $\nabla^i = g^{ij}\partial/\partial Q^j$, there are implicit summations over repeated indices.

The total wavefunction can now be expanded over other sets of electronic basis functions, the so-called diabatic representations:

$$\Psi(Q;\text{electrons}) = \sum_{\alpha'=1}^{\nu} \xi_{\alpha'}(Q,\text{electrons})\eta_{\alpha'}(Q)\,. \quad (11)$$

The transformation from the adiabatic basis set to the new one is done with an orthogonal matrix $\mathbf{G}(q)$ independent of the Euler angles:

$$\phi_\alpha(Q;\text{electrons}) = \sum_{\alpha'=1}^{\nu} G_{\alpha\alpha'}(q)\xi_{\alpha'}(Q;\text{electrons})\,. \quad (12)$$

For $\Psi(Q;\text{electrons})$ not to be changed in the transformation, the same matrix $\mathbf{G}(q)$ relates the adiabatic and the new nuclear functions:

$$\chi_\beta(Q) = \sum_{\alpha'=1}^{\nu} G_{\beta\alpha'}(q)\eta_{\alpha'}(Q)\,. \quad (13)$$

By application of the rule on differentiation of products, and after some calculation, eq. (10) becomes:

$$\sum_{\alpha'=1}^{\nu}\Bigg\{G_{\beta\alpha'}T^{nu}\eta_{\alpha'} + (E_\beta - E)G_{\beta\alpha'}\eta_{\alpha'} - \hbar^2\Bigg[g^{ij}\frac{\partial G_{\beta\alpha'}}{\partial Q^j} + \sum_{\alpha=1}^{\nu} {}^{\beta\alpha}T^i(Q)G_{\alpha\alpha'}\Bigg]\nabla_i\eta_{\alpha'} + \Bigg[[T^{nu}G_{\beta\alpha'}] + \sum_{\alpha=1}^{\nu}[{}^{\beta\alpha}T^{nu}(Q) - \hbar^2 {}^{\beta\alpha}T^i(Q)\nabla_i]\,G_{\alpha\alpha'}\Bigg]\eta_{\alpha'}\Bigg\} = 0\,. \quad (14)$$

Matrix G is chosen so that the coefficient of $\nabla_i\eta_{\alpha'}$ in eq. (14) is identically zero:

$$\nabla^i G_{\beta\alpha'} + \sum_{\alpha=1}^{\nu} {}^{\beta\alpha}T^i(Q)G_{\alpha\alpha'} = 0\,. \quad (15)$$

This particular choice is the same as the one of Baer [2–6]. Indeed, by introducing matrix elements of the type:

$${}^{\beta\alpha}T_j^{(1)}(Q) = \langle\phi_\beta(Q;\text{electrons})|\nabla_j\phi_\alpha(\phi;\text{electrons})\rangle\,,$$

identical with those defined in eq. (8) of ref. [2], and by factorization of $g^{ij}(q)$, eq. (15) results in:

$$\nabla_j G_{\beta\alpha'} + \sum_{\alpha=1}^{\nu} {}^{\beta\alpha}T_j^{(1)}(Q)G_{\alpha\alpha'} = 0\,, \quad (16)$$

which strictly is the same as eq. (16) in ref. [2]. In matrix notation:

$$\nabla_j\mathbf{G} + \mathbf{T}_j^{(1)}(Q)\mathbf{G} = 0\,. \quad (17)$$

Eq. (17) is also the same as eq. (1). Baer has algebraically demonstrated that this matrix equation admits a solution (which is an orthogonal matrix) under a necessary and sufficient condition:

$$\partial\mathbf{T}_j^{(1)}/\partial Q^i - \partial\mathbf{T}_i^{(1)}/\partial Q^j = [\mathbf{T}_j^{(1)}, \mathbf{T}_i^{(1)}] \quad \text{for every pair } (Q^i, Q^j; i, j = 1, 2,..., N) \quad (18)$$

(see eqs. (17) and (16) in ref. [2] and eq. (4.18) in ref. [3]). There is thus no going back on it here.

In the two-state approximation, this condition becomes:

$$\frac{\partial\mathbf{T}_j^{(1)}}{\partial Q^i} - \frac{\partial\mathbf{T}_i^{(1)}}{\partial Q^j} = 0 \quad (i, j = 1, 2...N)\,, \quad (19)$$

since two 2 × 2 antisymmetric matrices commute (see eq. (4.22) in ref. [3]). Now:

$$\partial^{\beta\alpha}T_j^{(1)}/\partial Q^i - \partial^{\beta\alpha}T_i^{(1)}/\partial Q^j$$

$$= \langle \partial\phi_\beta/\partial Q^i | \partial\phi_\alpha/\partial Q^j\rangle - \langle \partial\phi_\beta/\partial Q^j | \partial\phi_\alpha/\partial Q^i\rangle \quad (20)$$

(cf. eq. (1.9) in ref. [2]). The rhs of eq. (20) is clearly zero for $\alpha = \beta$. For $\alpha \neq \beta$, and if the two-state problem involves real electronic wavefunctions, each Dirac bracket in eq. (20) is equal to zero as a consequence of the completeness relation:

$$\langle \partial\phi_\beta/\partial Q^j | \partial\phi_\alpha/\partial Q^i\rangle$$

$$= -\sum_{\gamma=1}^{?} \langle \phi_\gamma | \partial\phi_\beta/\partial Q^j\rangle \langle \phi_\gamma | \partial\phi_\alpha/\partial Q^i\rangle .$$

Therefore, in case of a two-state problem, eq. (17) always admits an orthogonal solution matrix, $\mathbf{G}(q)$.

From the fact that, in this case,

$$\mathbf{T}_j^{(1)}(q) = \begin{bmatrix} 0 & -g_j(q) \\ g_j(q) & 0 \end{bmatrix} \quad (j = 1, 2...N) , \quad (21)$$

where

$$g_j(q) = \langle \phi_2(Q) | \nabla_j | \phi_1(Q)\rangle \quad (j = 1, 2...N) , \quad (22)$$

and

$$\mathbf{G}(q) = \begin{bmatrix} \cos\theta(q) & \sin\theta(q) \\ -\sin\theta(q) & \cos\theta(q) \end{bmatrix} , \quad (23)$$

the two sides of eq. (17) are, respectively,

$$\nabla_j \mathbf{G} = \begin{bmatrix} -\sin\theta\ \nabla_j\theta & \cos\theta\ \nabla_j\theta \\ -\cos\theta\ \nabla_j\theta & -\sin\theta\ \nabla_j\theta \end{bmatrix}$$

$$(j = 1, 2...3l - 6) , \quad (24)$$

and

$$\mathbf{T}_j^{(1)}\mathbf{G} = \begin{bmatrix} \sin\theta\ g_j & -\cos\theta\ g_j \\ \cos\theta\ g_j & \sin\theta\ g_j \end{bmatrix}$$

$$(j = 1, 2...3l - 6) . \quad (25)$$

Clearly, the particular choice of diabatic states asociated with the transformation matrix defined in eq. (17) – which is the one advocated by Baer [2–5,9] – implies that:

$$g_j(q) = \nabla_j\theta(q) = \partial\theta(q)/\partial q^j$$

$$(j = 1, 2...3l - 6) . \quad (26)$$

This set of partial differential equations (26) is well adapted, *in the two-state approximation,* to numerical calculations to derive $\theta(q)$ and $\mathbf{G}(q)$.

A last point is to understand why, in the general multistate case, this particular choice of diabatic representation is especially interesting. For this, it can be (quite tediously!) demonstrated that the quantity

$$[T^{nu}G_{\beta\alpha'}] + \sum_{\alpha=1}^{\nu} [{}^{\beta\alpha}T^{nu}(Q) - \hbar^{2\beta\alpha}T^i(Q)\nabla_i] G_{\alpha\alpha'}$$

appearing in eq. (14) vanishes identically and hence eq. (14) becomes, after multiplication on the left by $\Sigma_\beta G_{\beta'\beta}$,

$$T^{nu}\eta_{\beta'} + \sum_{\alpha'=1}^{\nu} W_{\beta'\alpha'}(q)\eta_{\alpha'} = 0 , \quad (27)$$

where

$$W_{\beta'\alpha'}(q) = \sum_{\beta=1}^{\nu} G_{\beta'\beta}(q)[E_\beta(q) - E]\, G_{\beta\alpha'}(q) . \quad (28)$$

Eqs. (27) and (28) constitute the diabatic version (i.e. in which all the coupling effects are of a potential nature since $\mathbf{W}(q)$ is no longer diagonal and its diagonal terms may cross each other) of eq. (10) within the adiabatic representation (i.e. in which the potential is diagonal and all the coupling effects are of a kinetic nature since ${}^{\beta\alpha}T^{nu}(Q)$ and ${}^{\beta\alpha}T^i(Q)$ are non-diagonal matrices).

Apart from these remarks, the quantal eq. (27) is very interesting as it allows one to establish the validity of a semiclassical model based on trajectories driven either by diabatic potential energy surfaces or adiabatic surface plus surface hoppings, *under the only condition that the kinetic energy (T^{nu}) of the hamiltonian used is correctly expressed according to the set of coordinates (either cartesian or curvilinear) used to describe the nuclear motion* [18].

All the other remarks made by Baer [2] concerning the diabatic representations remain valid within the generalized context of the present article.

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